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Ultrafine $MnFe_2O_4$ powder preparation by combusting the coprecipitate with and without Mg^{2+} or Zn^{2+} additives

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Ultrafine $MnFe_2O_4$ powder with its crystallites less than 100 nm was prepared using a combustion process. The coprecipitates containing the stoichiometric amount of Mn^{2+} and Fe^{3+} to form $MnFe_2O_4$ were prepared by dissolving the required metallic nitrates in de-ionized water and adding NH_4OH to adjust the pH of the solutions to 9. The collected dried precipitates were then heated up to predetermined temperatures and then quickly contacted with the acetone spray. Upon contacting with the heated precipitates, the acetone spray was ignited. The combustion of acetone caused the precipitates to form crystalline $MnFe_2O_4$ without chemical segregation. The crystallinity of $MnFe_2O_4$ powder so obtained depended on the ignition temperature of acetone spray. $MnFe_2O_4$ powder obtained at acetone ignition temperature of 773 K had higher crystallinity than that obtained at acetone ignition temperature of 523 K. The presence of a small amount of Mg^{2+} or Zn^{2+} in the composition of the coprecipitates promoted the mobility of constituent ions of the combusted powder and resulted in bigger $MnFe_2O_4$ crystallites at a lower acetone ignition temperature.

I. INTRODUCTION

Ferrites with an inverse spinel molecular structure have soft magnetic properties and are important components in the electronic industries. The quality and performance of ferrite products are greatly influenced by their microstructures. To have a better-controlled microstructure, the ferrite powder used in production should have the characteristics of high chemical homogeneity, ultrafine sizes with narrow size distribution, spherical-like shapes, and high sinterability. Several nonconventional routes for high-quality ferrite powder preparation have been used or are under development, such as the sol-gel method,[1] the hydrothermal method,[2] the aerosol method,[3–5] and the coprecipitation method.[6–11] Among them, the coprecipitation technique, because of its easy operation and because it is ready for mass production, is the most common one adopted in the production of ferrite powder. The coprecipitation technique used in preparing ferrite powder involves preparation of homogeneous solution that contains the required ratio of cations, precipitation of insoluble precursors of the ferrites by adding precipitating agents, separation of the solid precipitates from the liquid solution, removal of the soluble residuals by washing and drying, and formation of the ferrite powder by pyrolysis. In preparing ferrite powder with Mn^{2+}, special care must be taken to avoid the oxidation of divalent manganese ions during preparation because Mn^{2+} is unstable in air. The oxidation of Mn^{2+} would result in phase separation and make the formation of Mn-ferrites difficult. Chaudhuri and Roy[12] prepared manganese ferrite by firing the corresponding coprecipitates up to 1573 K and then cooling down the

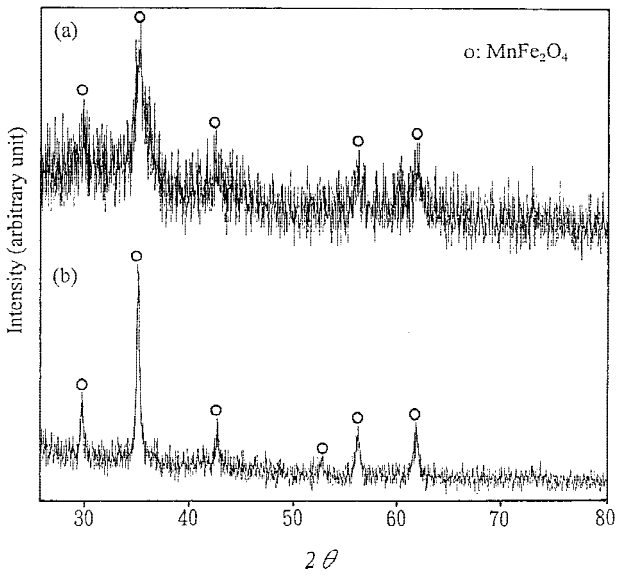

FIG. 1. XRD patterns for the combusted specimens (without any additives) obtained by igniting the acetone spray at (a) 523 K and (b) 773 K.

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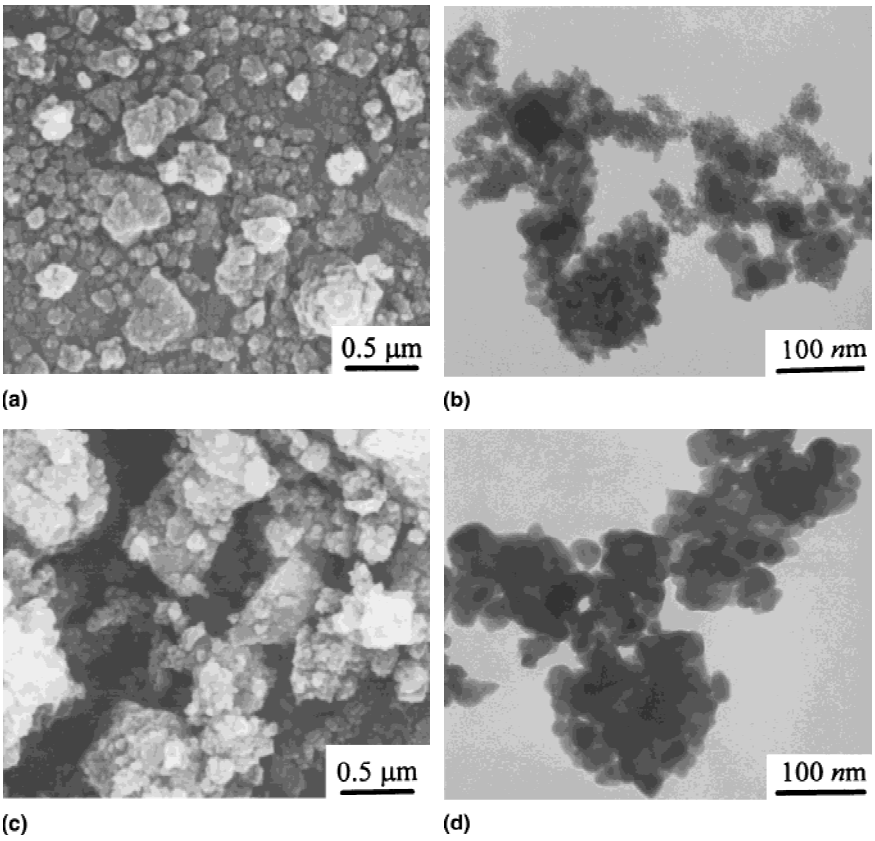

FIG. 2. Photomicrographs for the combusted specimens (without any additives) obtained by igniting the acetone spray at 523 K: (a) SEM and (b) TEM, and by igniting the acetone spray at 773 K: (c) SEM and (d) TEM.

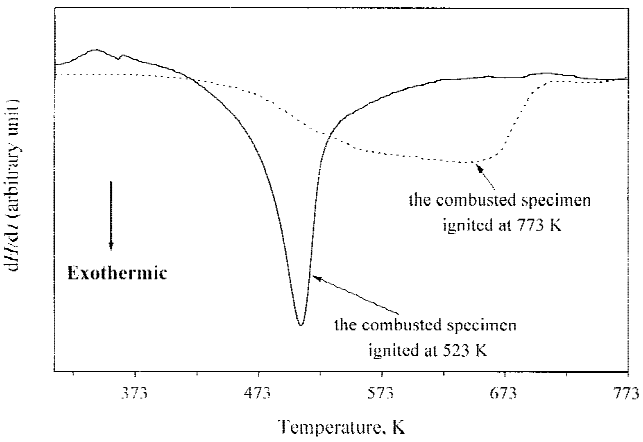

FIG. 3. DSC curves for the combusted specimens (without any additives) obtained at two different acetone ignition temperatures (heating rate 5 K/min).

specimen in a stream of nitrogen. Bakare *et al.*[13] and Sankarshana Murthy *et al.*[14] used stabilized MnO to prepare the required Mn-ferrites. On the other hand, Tang *et al.*[15] treated the coprecipitates with a digestion process to produce fine $Mn_xFe_{3-x}O_4$ ($0.2 < x < 0.7$) powder. To avoid the oxidation of Mn^{2+} during preparation and to shorten the production time, in this work a combustion treatment on the corresponding coprecipitates was introduced to provide an alternative way to prepare ultrafine $MnFe_2O_4$ powder. Moreover, the effects of Mg^{2+} and Zn^{2+} additives on the crystallinity of resultant $MnFe_2O_4$ particles were also investigated.

II. EXPERIMENTAL PROCEDURE

All chemicals used in this study were reagent purity and were used without further purification. $Mn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and Mg^{2+} or Zn^{2+}-nitrate hexahydrate (the additives) in molar ratios of 1:2:x (where $x = 0$, 0.001, 0.005, 0.02, and 0.05) were dissolved in de-ionized water to form aqueous solutions of 0.15 M. $NH_4OH_{(aq)}$ (concentration: 29.8 wt%) was then dropped into the solution, with continuous stirring, until the pH of the solution reached 9. Adding ammonium hydroxide caused the formation and precipitation of insoluble solids (the corresponding metallic hydroxides) and adjusting the solution to basic conditions was to assure the completion of precipitation. The collected precipitate was washed with de-ionized water, filtered with 0.2-μm membranes, and then dried at 353 K. After grinding, the dried specimen was then thermally treated in an oven at 523 K or 773 K for 1 h, followed by a

combustion process. It is to be noted that setting the oven temperature to 523 K or higher is to assure the decomposition of precipitates to form the corresponding oxides. The combustion process was carried out by quickly removing the heated specimen from the oven and contacting the specimen with the acetone spray. The elevated temperatures of the heated specimens ignited the acetone spray and caused the specimens to undergo vigorous burning. For the sake of comparison, another set of dried specimens was heated in the oven at the temperatures mentioned above and then naturally cooled down in air to room temperature. In the following discussion, the fired specimen is used to represent the powder that was obtained from an air heating and cooling procedure and the combusted specimen is then used to stand for those obtained by contacting the heated specimen with the acetone spray. The specimens obtained from these two processes were analyzed using differential scanning calorimetry (DSC; DSC 200, Netzsch), x-ray diffraction (XRD; M03X-HF, Mac Science), scanning electron microscopy (SEM; S-800, Hitachi), and transmission electron microscopy (TEM; H-7000, Hitachi), to determine the characteristics of specimens. The effects of Mg^{2+} and Zn^{2+} additives on the resultant $MnFe_2O_4$ particles were also examined by comparing the characteristics of $MnFe_2O_4$ powder with and without Mg^{2+} or Zn^{2+} additions. The resulting results are discussed.

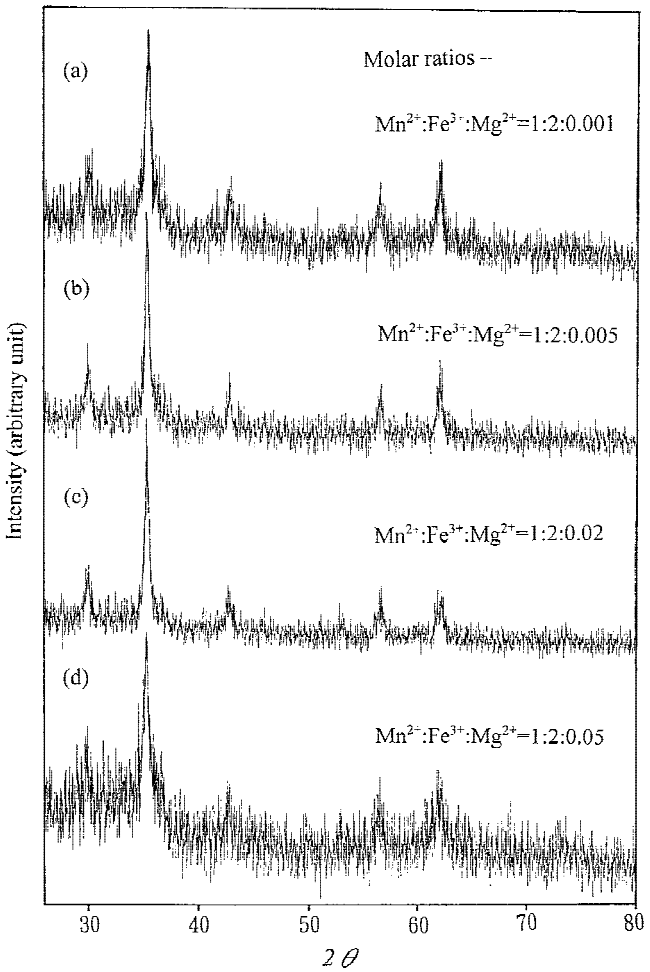

FIG. 4. XRD patterns for the combusted specimens with Mg^{2+} addition, obtained by igniting the acetone spray at 523 K.

III. RESULTS AND DISCUSSION

A. Air heating and cooling process

Regardless of compositions of the starting solutions and temperatures of the heat treatment, the fired specimens obtained by naturally cooling the heated specimens in air did not contain any crystalline phase of $MnFe_2O_4$. XRD examination showed that heated up to 773 K, the fired specimens with no Mg^{2+} or Zn^{2+} additions were

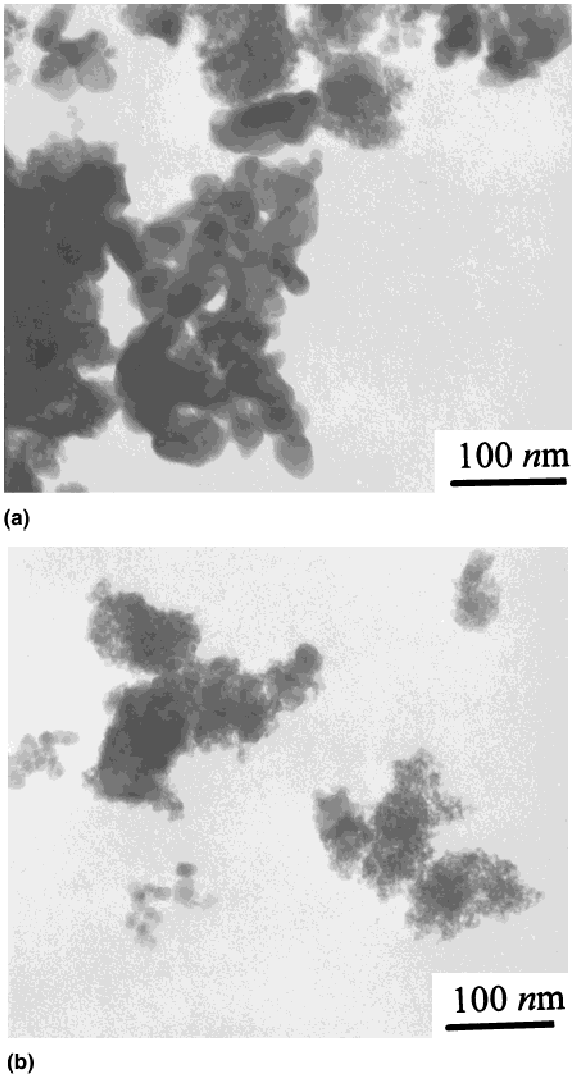

FIG. 5. TEM photomicrographs for the combusted specimens obtained at an acetone ignition temperature of 523 K. Molar ratios for the specimens (a) $Mn^{2+}:Fe^{3+}:Mg^{2+}$ = 1:2:0.001 and (b) $Mn^{2+}:Fe^{3+}:Mg^{2+}$ = 1:2:0.05.

noncrystalline materials; however, adding Mg^{2+} or Zn^{2+} to the compositions caused the formation of crystalline α–Fe_2O_3 at 773 K. It is to be noted that when the heating temperature was increased to 973 K, crystalline α–Mn_2O_3 phase, in addition to α–Fe_2O_3, was detected in the fired specimens for all compositions. Although the presence of small amount of Mg^{2+} or Zn^{2+} in the compositions could promote the crystallinity of the corresponding metallic oxide, it is difficult to prevent the oxidation of divalent manganese ions in an air heating and cooling process. To reduce manganese ions from Mn^{3+} to Mn^{2+} and/or to obtain the required $MnFe_2O_4$ phase, the combustion process mentioned previously was used in this study to produce ultrafine crystalline $MnFe_2O_4$ powder.

B. Combustion process

Figure 1 shows the XRD patterns of combusted specimens, containing no additives of Mg^{2+} or Zn^{2+}, obtained by igniting the acetone spray at 523 and 773 K, respectively. It was evident that all these combusted powders were composed of $MnFe_2O_4$ crystallites. By examining the broadness of XRD peaks, the combusted specimen obtained by igniting the acetone spray at 523 K contained very tiny $MnFe_2O_4$ crystallites. Increasing the ignition temperatures caused $MnFe_2O_4$ crystallites to grow bigger. All combusted specimens exhibited magnetic characteristics, which was observed by placing the powders in a magnetic field. Figure 2 gives the SEM and TEM photomicrographs of combusted specimens with ignition temperatures at 523 and 773 K, respectively. All combusted powders consisted of submicron agglomerated particles [Figs. 2(a) and 2(c)] and the sizes of crystallites were much less than 100 nm [Figs. 2(b) and 2(d)]. The TEM analysis gave the same conclusion as that obtained from the XRD analysis: The crystallites obtained at an ignition temperature of 773 K were much larger than

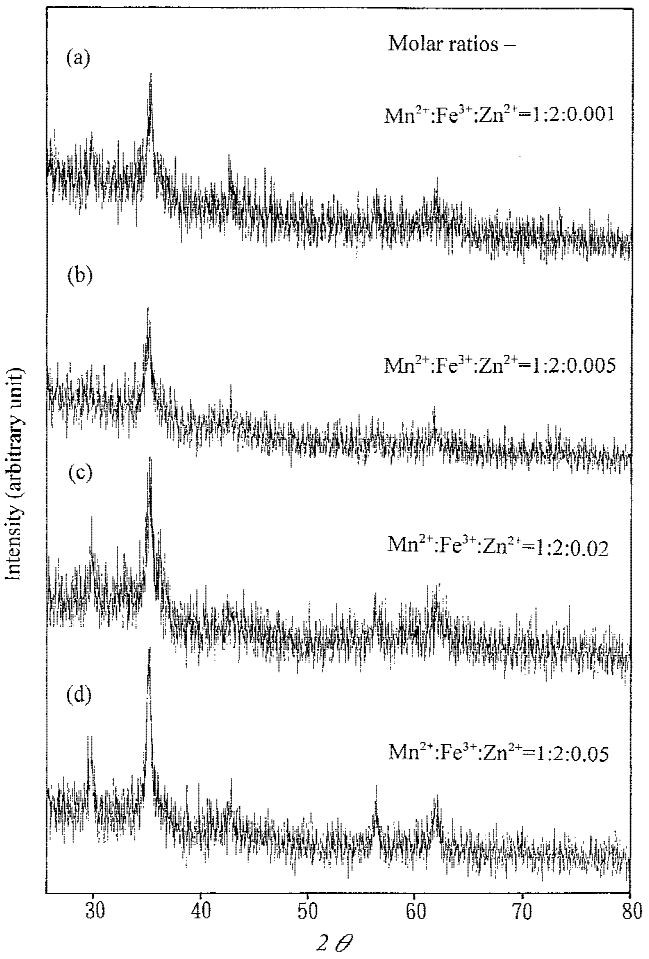

FIG. 6. XRD patterns for the combusted specimens with Zn^{2+} addition, obtained by igniting the acetone spray at 523 K.

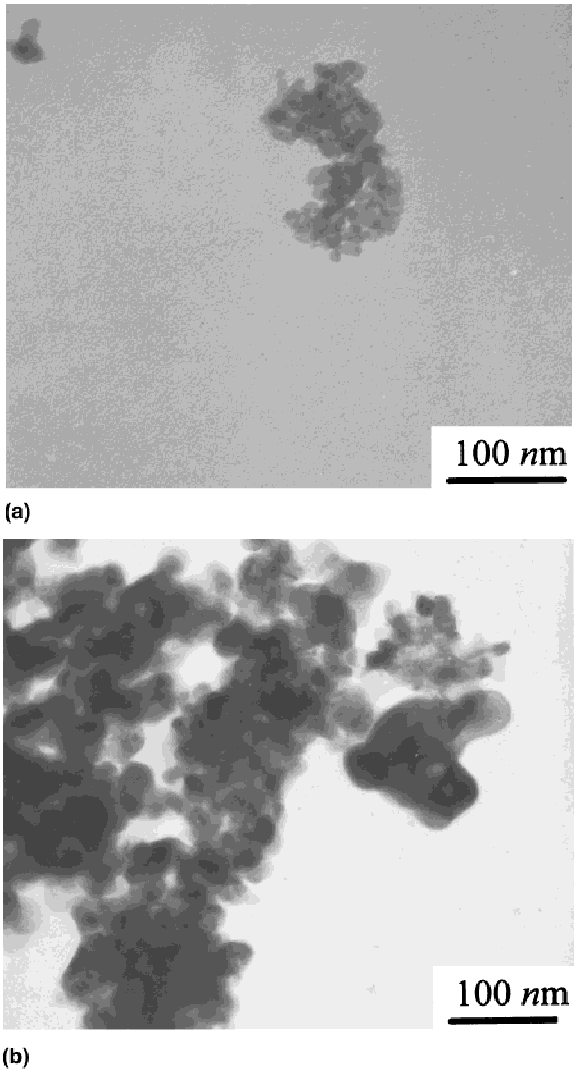

FIG. 7. TEM photomicrographs for the combusted specimens obtained at an acetone ignition temperature of 523 K. Molar ratios for the specimens (a) Mn^{2+}:Fe^{3+}:Zn^{2+} = 1:2:0.001 and (b) Mn^{2+}:Fe^{3+}:Zn^{2+} = 1:2:0.05.

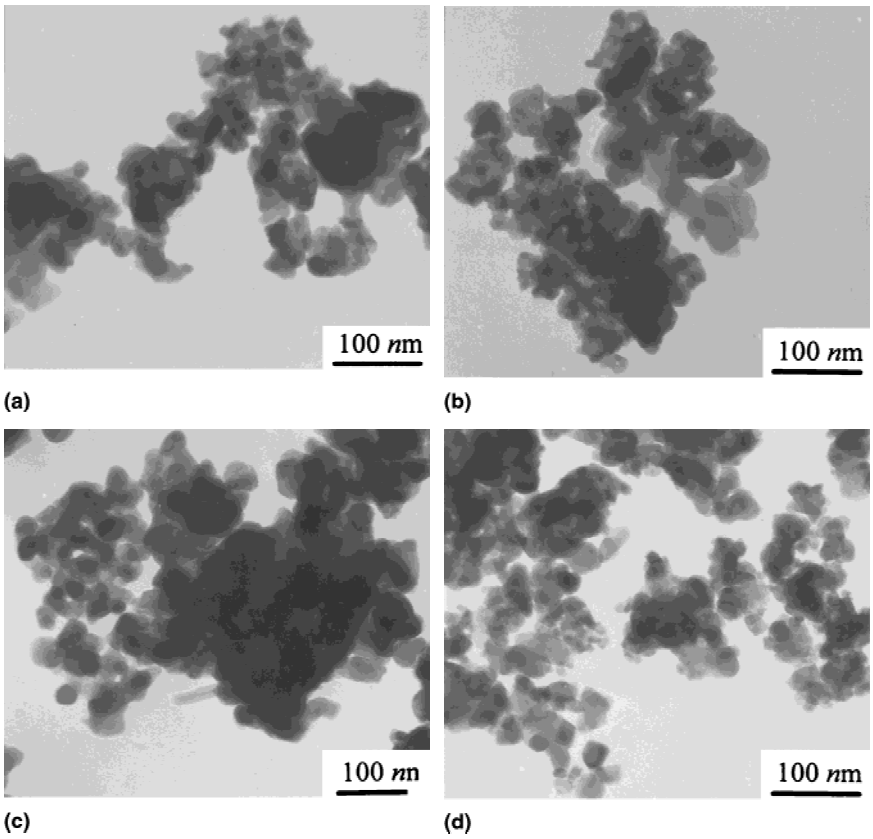

FIG. 8. TEM photomicrographs for the combusted specimens with a molar composition of: (a) Mn^{2+}:Fe^{3+}:Mg^{2+} = 1:2:0.001, (b) Mn^{2+}:Fe^{3+}:Mg^{2+} = 1:2:0.05, (c) Mn^{2+}:Fe^{3+}:Zn^{2+} = 1:2:0.001, (d) Mn^{2+}:Fe^{3+}:Zn^{2+} = 1:2:0.05, obtained by igniting the acetone spray at 773 K.

those at 523 K. By comparing the results for these combusted specimens with those for the fired specimens, it is suggested that the combustion of acetone, upon contact with the heated specimens, provides a high enough temperature environment for reducing manganese ions from Mn^{3+} to Mn^{2+} and/or to form manganese ferrite. Acetone spray ignited at higher temperatures instantly gives off more energy and results in the formation of larger $MnFe_2O_4$ crystallites.

Figure 3 gives the DSC curves of these combusted specimens (containing no additives) and reveals their thermal behavior. During heating in an air atmosphere, the combusted specimen experienced exothermic changes at temperatures between 398 and 598 K for the one igniting the acetone spray at 523 K and between 448 and 723 K for that igniting the acetone spray at 773 K. These specimens after DSC analysis were subjected to XRD analysis and the corresponding XRD patterns indicated that the powders were all composed of tiny crystallites of α–Mn_2O_3 and γ–Fe_2O_3. Accordingly, these exothermic changes were mainly due to the oxidation of divalent manganese ions and then the separation of chemical phases. The differences in temperature ranges of these exothermic changes were ascribed to the differences in crystallinity of the powders. $MnFe_2O_4$ powder with higher crystallinity is more stable in air.

To promote the crystallinity of $MnFe_2O_4$ in the combusted specimen, Mg^{2+} or Zn^{2+} were introduced into the composition of coprecipitates. Figure 4 is the XRD patterns for the combusted specimens, containing various amounts of Mg^{2+} additives, obtained by igniting the acetone spray at 523 K. Adding Mg^{2+} at amounts of 2% or less (with respect to the moles of manganese ions) into the compositions seemed to enhance the mobility of constituent ions and results in an increase of crystallinity of $MnFe_2O_4$. However, the combusted specimen with 5% Mg^{2+} addition did not show any distinguishable differences from that of the combusted specimen without additives [comparing Fig. 4(d) with Fig. 1(a)]. The TEM photomicrographs of the specimens shows the effects of Mg^{2+} additions on the crystallinity of combusted specimens. As concluded from the XRD analysis, the combusted specimen with 0.1% Mg^{2+} additions [Fig. 5(a)] was composed of larger $MnFe_2O_4$ crystallites than that of the specimens with 5% Mg^{2+} additions [Fig. 5(b)].

The effects of Zn^{2+} addition on the crystallinity of $MnFe_2O_4$ particles are shown in Fig. 6. More Zn^{2+} additions resulted in higher $MnFe_2O_4$ crystallinity of the combusted powder. Figure 7 shows the TEM photomicrographs for the combusted samples with 0.1% and 5% Zn^{2+} additions. These TEM photomicrographs confirm the conclusions drawn from the results of XRD analysis.

On the other hand, the combusted powders, regardless of types and amounts of the additive, were all composed of submicron primary particles with heavy agglomerations, which were evident from their SEM photomicrographs.

Like those observed for the combusted specimens without Mg^{2+} or Zn^{2+} additions, raising the ignition temperatures of acetone spray increases the degree of crystallinity and the size of crystallites of $MnFe_2O_4$ in combusted specimens. The TEM photomicrographs of combusted specimens (with Mg^{2+} or Zn^{2+} additions of 0.1% and 5%) obtained at an ignition temperature of 773 K are given in Fig. 8. By comparing Fig. 8 with Fig. 5 and Fig. 7, it is clear that when the ignition temperature of acetone spray increases to 773 K, the effects of types and amounts of the additive are less pronounced.

IV. CONCLUSIONS

Ultrafine $MnFe_2O_4$ powder with the corresponding crystallites less than 100 nm was prepared using a combustion process. The coprecipitated particles containing the stoichiometric amount of Mn^{2+} and Fe^{3+} to form $MnFe_2O_4$ were heated up and then brought in contact with the acetone spray, which resulted in the burning of acetone. The combustion of acetone spray instantly gave off a high enough energy to force the powder to form crystalline $MnFe_2O_4$. Raising the acetone ignition temperature increased the size of crystallites of the resultant $MnFe_2O_4$. The thermal stability of $MnFe_2O_4$ powder so obtained in an air atmosphere depended on the crystallinity of $MnFe_2O_4$; $MnFe_2O_4$ powder with a higher crystallinity showed a wider temperature range for thermal stability. The presence of small amount of Mg^{2+} or Zn^{2+} in the composition of coprecipitates promoted the mobility of constituent ions of the combusted powder and resulted in bigger $MnFe_2O_4$ crystallites at a lower acetone ignition temperature.

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